

THE VACUUM SPARK SPECTRUM OF ZINC

A DISSERTATION

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I. INTRODUCTION

The research constituting the body of this paper was undertaken for the purpose of producing in the spectrum region usually covered by the quartz spectrograph, zinc spectrum lines corresponding to higher energy levels than are reached by such means of excitation as the flame, arc, or ordinary spark. During the fifteen years previous to the time this work was done four sources of excitation had been used with notable success in reaching high atomic energy levels. These sources were:

1. The electric furnace developed by A. S. King¹ in 1908.
2. The vacuum arc of Fabry and Perot² (1900).
3. The "exploded wire" developed by J. A. Anderson³ in 1920.
4. The vacuum spark suggested by Rowland and again by Wood⁴ in 1897.

II. THE VACUUM SPARK

This method of excitation consists in producing a highly condensed spark discharge between electrodes in a high vacuum. Due to the great field intensity necessary to produce a discharge under such conditions atoms of the electrode material are removed and very highly ionized, partly by the field and partly by the high temperature. The comparatively low pressure at which the discharge takes place tends to produce sharp spectrum lines which may be measured with accuracy.

It was in 1918 that Millikan and Sawyer⁵ demonstrated the utility of the vacuum spark for reaching high atomic energy levels when they discovered 57 new zinc lines in the region between 928A and 2138A. In 1919 Sawyer⁶ found 115 zinc lines and 15 carbon lines between 316A and 2139A. In 1921 Millikan, Bowen and Sawyer⁷ found 210 new iron lines in the region 271A to 2152A; 75 lines for carbon between 360A and 1931A, and 78 lines for

nickel in the region 731A to 1859A.

In 1922 Miss Carter⁸ published the results of her work with the vacuum spark. For calcium and magnesium she found their ordinary spark lines, while for cadmium, titanium and iron she found the arc lines more prominent than the ordinary spark lines. From the literature it seems that Miss Carter is the only one to obtain negative results with the vacuum spark.

J. A. Anderson⁹ found a total of 850 lines in the vacuum spark spectrum of calcium of which 46 were known calcium lines. Sawyer and Paton¹⁰ worked with silicon in the region 2100A to 6700A and found a total of 300 vacuum spark lines, 80 of which had been found before. All the lines used by Fowler in working out the series classification for silicon were found by Sawyer and Paton. In 1923 Hutchinson¹¹ found a large number of zinc lines in the region 467A to 2145A. His accuracy seems to have been impaired by plate shift. In the same year R. W. Wood¹² reported about 60 new lines in the spectrum of zinc in the region 832A to 1918A.

A study of the results obtained with the vacuum spark shows that in addition to the excitation of new spectrum lines it suppresses (sometimes to total extinction) the flame and arc lines of the elements. Many of the lines discovered by this method of excitation have been fitted into the series spectra of the ionized elements. The effectiveness of the vacuum spark in such works as those mentioned above constituted the basis for its use in the research presented in this paper.

III. PREVIOUS WORK ON ZINC

A complete bibliography of the spectrographic work done on zinc before 1912 is given by Kayser.¹³ A few of the papers in Kayser's list might be mentioned here because of their connection with

this work. In 1884 Hartley and Adeney¹⁴ sparked zinc in air and found 108 lines; most of which are not found in the arc, and some of which had not been discovered until the work being described in this paper was done. Their wave lengths were so poor that in many cases the identity of the lines is uncertain. In 1905 Steinhausen¹⁵ reported his work on the enhanced lines of various elements including zinc. He used a one meter grating and a strongly condensed spark. Some of his lines had not been listed in other reports previous to this one. The same is true of the work of Lockyer¹⁶ in 1906. Two accurate pieces of work on the spark spectrum of zinc were done in 1911 and 1912 by Exner and Haschek¹⁷ and by Eder and Valenta.¹⁸ Although the wave lengths given in these two reports agree very well their utility is somewhat impaired by the rather inaccurate standards available at that time. In 1913 Huppers¹⁹ reported his work with the arc spectrum of zinc between 2100A and 3300A. He used a quartz spectrograph and gave his wave lengths in both Rowland and International units.

Previous to the time this work was completed (1924) the greater part of the recent work on zinc had been done with the vacuum arc and spark in the region below 2000A. In 1909 Handke,²⁰ using a Schumann spectrograph, measured 52 zinc lines between 1632A and 1987A. Later workers do not agree very well with his wave lengths, largely because at that time standards were too scarce in that part of the spectrum to permit accuracy with a prism. With hydrogen lines as standards Wolfe,²¹ in 1913 measured 11 zinc lines between 1376A and 1650A using both grating and fluorite spectrographs. In 1916 Saunders²² reported his work with the vacuum arc and ordinary spark spectra of zinc in the region 1673A to 2253A. He used a vacuum grating spectrograph. The wave lengths of the 25 lines he reported do not agree with those of Handke.

In 1919 Sawyer⁶ reported 115 zinc lines in the region 316A to 2139A. He used a vacuum grating spectrograph and the vacuum spark. In the same year McLennan, Ainslie and Fuller²³ studied the vacuum arc spectrum of zinc using a fluorite spectrograph of simple design.

Between 1445A and 2025A they measured 11 zinc lines four of which were new. As already mentioned Hutchinson¹¹ reported a large number of zinc lines which he found with the vacuum spark in the region 465A to 2145A. He did not claim great accuracy because of lack of definition probably due to plate shift. As the result of his work in the region 832A to 1918A with a vacuum grating spectrograph and the vacuum spark as a source R. W. Wood,¹² in 1923 reported 60 zinc lines many of which were new.

A glance at the above summary shows that previous to 1924, neither the vacuum arc nor spark had been used as a means of exciting the zinc spectrum above 2100A. It was expected that a careful investigation of the region above 2300A would produce lines that might be of considerable use in working out the series classification for zinc.

IV. APPARATUS

THE QUARTZ SPECTROGRAPH was built in the shop of the Physics Department and was patterned after the design of Fabry and Buisson.²⁴ The main feature of this design consists in the use of a platinum sputtered concave mirror as a collimating means. In order to minimize astigmatism as far as possible the slit was mounted in the housing just over the prism. The other parts of this instrument were such that by careful adjustment the entire spectrum region between 2000A and 4000A could be brought into good focus on one plate.

THE SPARK BOX was made by sealing three tubes to a thick-walled, spherical, two-liter pyrex flask. The neck of the flask and the three tubes were in the same plane and located 90 degrees apart. One of the tubes at right angles to the neck was about 22 inches long and about 2-1/2 inches in diameter. To its outer end was cemented a quartz window; which, due to its distance from the spark in the body of the flask, remained free from any film due to sputtering of metal from the electrodes. The other two tubes were about 12 inches long and their outer ends were tapered and ground to fit hollow glass stoppers which extended inwardly

nearly to the center of the flask. Heavy tungsten wires sealed into the hollow stoppers extended to the center of the flask and carried the electrodes. The neck of the flask was connected to a two-stage mercury vapor pump through a liquid air trap.

THE ELECTRODES were cut from highly purified zinc rods. Chemical analysis gave as impurities: iron, .0063%; lead, a trace; cadmium, a trace; and no arsenic. Very few impurity lines were found in the spectrograms.

THE PHOTOGRAPHIC PLATES were Cramer contrast process plates sensitized for the ultra violet by coating them with a thin layer of Nujol which was washed off with acetone before development.

THE GENERAL ARRANGEMENT OF THE APPARATUS was such that a glass plate, oil-immersed condenser of about a quarter microfarad capacity was charged to about 70 or 80 kilovolts by means of a 60 cycle transformer. This condenser was discharged through an external gap in series with the one in the spark box. The leads in the condenser discharge circuit were stranded and as short as possible. By means of a rotating switch in series with the primary of the transformer the spark was turned on once each second and allowed to continue one sixth of a second. This procedure allowed the pumps time to dispose of the gases evolved from the electrodes.

The time of exposure was from 15 to 45 minutes. This represents the time during which radiation from the spark entered the spectrograph slit, although the total lapsed time required to obtain a plate was from 3 to 14 hours. During each exposure the temperature of the laboratory was kept constant within a degree or two.

THE MEASUREMENT OF THE PLATES was done in a small room in which the temperature was constant within half a degree. The arc lines of iron were used as standards. Below 3370A the wave lengths obtained by Burns²⁵ with an 18 foot grating were used; while above 3370A the wave lengths given by St. John and Babcock²⁶ as well as by Burns²⁵ were used. They worked with a large grating as well as an interferometer. These wave length standards were later found to agree very well with

the work of Meggars, Kiess and Burns²⁷ at the Bureau of Standards.

V. ACCURACY

By using nearly all the iron lines in the spectrum region (2300A to 4000A) covered in this research, and, by using the interpolation formula of Hartmann it was possible to obtain wave-length measurements accurate to within a few hundredths of an Angstrom. This statement is substantiated by:

1. The closeness with which the measurements of the standard iron lines followed the Hartmann interpolation curve.
2. The good agreement between this and other researches on the wave lengths of the impurity lines.
3. The close agreement between the measurements made from as many as six plates for many of the new lines.

Such accuracy is partly due to the sharpness of the lines and partly to the fact that the position of each line on each plate was determined as the mean of six to fifteen settings of the comparator. To guarantee against plate shift several plates were exposed to the radiation emitted from the vacuum spark when one electrode was pure iron and the other zinc. In this way the standard iron lines were found distributed among the zinc lines.

VI. RESULTS

Although this work was completed in 1924 it has not been published except for an abstract.²⁸ Recently L. and E. Bloch²⁹ have published the results of their work with the vacuum spark spectrum of zinc in the region 2586A to 4039A. In the following table their lines are tabulated for comparison with those measured in this research. They claim an accuracy of a tenth of an Angstrom in the short wave region and a few tenths of an Angstrom in the long wave portion. They state that lines given with an intensity of "0" are somewhat doubtful.

VII. TABLE OF WAVE LENGTHS

<u>L. and E. Bloch</u>	<u>Present Research</u>	<u>L. and E. Bloch</u>	<u>Present Research</u>
	5 2398.83		20 2557.94
	6 2401.48		5 2570.68
	10 2405.20		4 2571.33
	12 2418.73		5 2575.44
	6 2420.78		12 2575.86
	12 2423.35		3 2578.59
	6 2434.32		4 2586.12
	5 2437.53	2 2586.90	2 2586.80
	6 2438.21	3 2588.37	3 2588.09
	15 2441.99	3 2590.07	2 2589.87
	6 2444.94	---	4 2590.45
	4 2448.25	4 2591.40	3 2591.29
	10 2450.33	---	7 2592.99
	5 2451.23	---	3 2597.14
	4 2456.00	---	3 2603.97
	5 2460.44	1 2605.73	1 2605.33
	12 2462.06	0 2606.63	---
	3 2462.56	2 2607.19	---
	6 2463.68	2 2609.27	---
	12 2467.05	3 2610.67	2610.61
	7 2468.90	3d 2613.02	2 2612.79
	8 2472.64	0 2614.37	---
	12 2473.31	2615.94	4 2615.86
	3 2473.76	6d 2618.76	3 2618.52
	3 2478.55	---	3 2619.02
	5 2480.22	4d 2621.85	3 2621.72
	10 2484.55	---	3 2622.08
	8 2486.17	---	3 2627.23
	14 2486.89	1 2628.24	2 2628.35
	8 2490.79	1 2629.12	2 2629.37
	8 2492.07	1 2629.94	2 2630.05
	6 2496.16	1 2630.89	---
	5 2497.13	2d 2632.53	2 2632.39
	5 2497.87	---	2 2632.96
	20 2501.99	1d 2633.42	2 2633.59
	1 2503.25	3 2636.16	3 2636.26
	1 2504.13	3d 2637.86	---
	5 2508.12	5 2640.26	5 2640.37
	15 2509.07	4 2641.75	2 2641.67
	1 2509.83	3 2644.48	3 2644.59
	5 2514.66	3 2645.52	3 2645.62
	8 2515.08	1 2646.72	---
	5 2520.43	1 2647.85	---
	14 2522.08	6 2649.76	5 2650.03
	14 2527.06	6 2651.06	5 2651.07
	4 2527.94	---	2 2651.57
	3 2528.63	1 2653.07	2 2653.10
	6 2532.15	0 2654.06	---
	8 2533.36	4 2655.27	5 2655.37
	5 2534.77	---	4 2657.22
	7 2535.92	---	8 2658.15
	4 2539.43	---	3 2658.63
	4 2546.21	6 2659.51	4 2659.65
	4 2546.67	0 2661.53	---
	6 2552.54	4 2663.43	3 2663.59
	5 2553.31	4 2664.82	5 2664.92
	3 2554.34	5 2666.27	4 2666.25

L. and E. Bloch		Present Research		L. and E. Bloch		Present Research	
---		3	2666.64	---		3	2857.77
4	2668.00	4	2668.28	0	2865.86	---	
0	2669.32	1	2669.32	---		3	2875.70
2	2670.42	---		---		2	2881.35
5	2673.00	4	2673.25	---		2	2887.37
Od	2674.90	---		3	2916.18	---	
02	2675.60	2	2676.02	---		4	2942.26
1	2678.42	2	2678.74	1	2945.56	---	
2	2679.29	3	2679.48	0	2950.07	---	
---		3	2680.62	1	2952.95	---	
---		3	2681.13	0	2967.15	---	
---		3	2682.80	0	2973.06	---	
8	2683.11	3	2683.34	0	2985.50	---	
2	2684.87	---		2	2990.67	---	
---		2	2685.84	---		2	2997.99
2d	2687.82	---		---		2	3024.47
---		2	2688.20	---		2	3043.87
2	2689.64	---		---		3	3096.94
0?	2691.04	---		2	3129.40	---	
5	2692.36	3	2692.61	---		2	3159.13
7	2694.08	3	2693.91	---		3	3171.25
---		3	2694.55	---		3	3172.24
---		4	2696.00	---		4	3175.95
---		6	2699.21	---		2	3177.26
---		3	2701.17	1	3192.06	1	3192.17
---		2	2701.62	---		4	3196.20
1	2704.21	2	2704.33	---		1	3209.79
3	2705.52	3	2705.65	---		1	3263.74
2	2706.71	3	2706.83	---		1	3266.34
5	2708.47	3	2708.68	---		6	3299.50
4	2709.44	3	2709.57	---		6	3306.13
Od	2711.38	---		---		6	3334.92
ld	2718.60	---		---		1	3360.20
1	2719.65	2	2719.89	---		1	3371.10
---		7	2720.82	---		3	3373.44
---		2	2722.43	---		3	3382.88
4	2727.27	2	2727.30	---		3	3393.66
3	2733.85	3	2734.16	---		3	3403.75
0	2735.92	---		1	3410.43	1	3410.24
0	2738.78	---		0	3413.03	---	
2	2740.84	2	2740.97	1	3416.91	---	
2	2746.42	---		0	3419.01	---	
1	2750.39	---		0	3423.32	---	
2	2755.00	2	2755.23	0	3425.77?	3	3426.09
---		2	2758.80	1	3428.90	3	3428.86
2	2761.20	2	2761.31	3d	3434.51	3	3434.68
2	2763.76	2	2763.97	0	3439.56	---	
---		4	2779.01	---		2	3444.70
---		4	2782.82	3d	3446.10	2	3446.04
2d	2785.95	3	2786.09	0	3450.67	---	
0	2793.23	---		4	3456.11	2	3456.36
0	2809.20	---		---		3	3462.35
0	2820.85	2	2821.06	0	3466.10	---	
---		2	2832.94	0	3468.72	---	
---		2	2838.72	2	3470.85	1	3470.96
---		4	2845.25	2	3472.47	---	
---		1	2849.26	1	3475.18	1	3475.24
---		2	2853.18	1	3478.86	1	3478.94
---		2	2854.14	0	3481.45	---	

L. and E. Bloch		Present Research		L. and E. Bloch		Present Research	
0	3484.44	2	3484.59	---	---	8	3748.54
---	---	5	3492.45	---	---	8	3755.27
1	3498.99	2	3499.36	---	---	10	3756.73
0	3500.99	---	---	2	3766.46	4	3766.63
1	3505.52	---	---	---	---	8	3770.98
---	---	3	3508.99	---	---	2	3775.81
---	---	3	3510.12	5	3776.27	7	3777.84
2	3512.78	3	3512.76	---	---	3	3778.26
2	3516.01	1	3515.71	---	---	7	3785.18
3	3520.04	2	3519.89	2	3789.13	3	3789.12
---	---	6	3529.48	---	---	8	3801.19
---	---	12	3530.88	---	---	2	3803.34
---	---	8	3536.88	3	3804.84	2	3805.06
---	---	8	3539.09	---	---	8	3806.32
0	3545.85	---	---	---	---	4	3810.80
---	---	4	3553.13	---	---	10	3812.90
---	---	1	3555.64	---	---	5	3823.05
1	3557.09	1	3556.91	---	---	10	3825.02
---	---	12	3562.51	---	---	11	3830.60
---	---	3	3576.27	---	---	2	3837.51
---	---	12	3580.79	---	---	14	3840.29
---	---	3	3587.44	---	---	2	3842.02
---	---	4	3589.59	3	3850.00	2	3849.98
---	---	3	3595.25	---	---	6	3859.88
4	3598.80	3	3598.85	---	---	3	3863.30
---	---	4	3601.20	6	3864.73	8	3864.97
---	---	3	3612.14	3	3869.24	3	3869.27
---	---	5	3613.26	---	---	3	3871.61
---	---	6	3614.39	3	3878.54	4	3878.48
---	---	6	3615.23	---	---	2	3882.12
---	---	8	3620.45	---	---	2	3883.94
---	---	12	3624.23	3	3885.76	2	3885.64
---	---	3	3630.09	1	3904.46	---	---
---	---	14	3632.02	3	3908.95	3	3908.89
---	---	8	3635.53	---	---	12	3912.12
---	---	12	3647.70	---	---	3	3914.88
---	---	2	3650.08	---	---	2	3921.05
---	---	3	3653.59	---	---	2	3924.50
---	---	6	3657.46	---	---	2	3928.22
---	---	8	3661.76	---	---	12	3935.24
---	---	15	3668.20	---	---	7	3938.90
---	---	8	3677.44	---	---	12	3943.21
---	---	8	3687.91	1	3955.42	2	3955.17
---	---	8	3693.43	---	---	5	3963.60
---	---	8	3695.19	---	---	14	3971.60
---	---	15	3703.61	---	---	2	3974.73
---	---	6	3705.79	2	3975.21	3	3975.37
---	---	2	3708.18	4	3982.35	6	3982.26
---	---	14	3713.67	---	---	12	3989.00
2	3717.35	3	3717.47	---	---	4	3996.81
---	---	15	3720.44	---	---	3	4001.20
---	---	3	3727.43	3	4006.73	4	4006.73
---	---	7	3730.38	3	4010.16	---	---
---	---	3	3732.74	3	4039.34	---	---
---	---	4	3745.20	---	---	---	---

VIII. SUMMARY

The lines in the foregoing table probably include, besides the doublets of singly ionized zinc, the spectrum of doubly ionized zinc. In working out the series for other elements in the singly ionized state the number of classified lines between 2000A and 4000A has always been less than a hundred for each element. It is probable therefore that of the 400 or more lines in the above table over 300 belong to the "many-lined" spectrum of doubly ionized zinc. As the result of a study of the Zeeman patterns for some of the prominent pairs in the line spectrum of zinc the pair 2025.49A and 2061A with a frequency separation of 872.2 have been shown to constitute the first member of the principal series. The same pair with negative sign together with 2558.01A and 2502.03A constitute the first two members of the sharp series. In the table given above 35 pairs were found having a frequency difference close to 872. Paschen³⁰ gives the pair 4924.16 and 4911.81 having a frequency separation of 51 as the first member of the Bergman Series. The above table contains 15 pairs having a frequency separation close to 51.

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